An XPS Investigation of Hydrothermal and Commercial Barium Titanate Powders

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Abstract

Hydrothermal and commercial barium titanate powders were examined for undesirable impurity phases. Compositional differences in the powder were evaluated using x-ray diffraction (XRD), x-ray fluorescence (XRF), and x-ray photoelectron spectroscopy (XPS). A barium-rich impurity phase, virtually undetectable by XRD, was detected via XPS. Barium impurity phase peaks were detected at binding energies > 1.5 eV higher than those characteristic of barium in a barium titanate bonding state for both the Ba 3d and Ba 4d transitions. Simple curve-fitting techniques were used to quantify the percentage of barium in a barium titanate bonding state versus another barium bonding state for each set of doublets. The barium impurity bonding state accounted for 20 - 50 mol% of the barium detected by XPS.

1. Introduction

Submicron, crystalline barium titanate powders can be hydrothermally synthesized from inexpensive, aqueous slurries of barium hydroxide and titanium dioxide precursors at temperatures near the boiling point of water in an ambient atmosphere. The synthesis proceeds according to the net reaction:

$$\text{TiO}_2 + \text{Ba(OH)}_2 \rightarrow \text{BaTiO}_3 + \text{H}_2\text{O}$$

To maximize conversion, an excess of barium hydroxide is necessary to force the reaction to go to completion. As in the processing of other chemically derived powders, a subsequent washing procedure is necessary following the synthesis of hydrothermal barium titanate to remove any excess reagent or other undesirable impurity phases from the product. In particular, excess barium hydroxide reagent must be removed to maintain a 1:1 Ba/Ti molar ratio and to prevent formation of barium carbonate upon contact with carbon dioxide in the atmosphere. However, excessive washing must be avoided, since a barium-deficient or titania-rich powder can result in excessive grain growth during firing. In addition, the hydrothermal slurries, which have a pH of 12-14 prior to washing, must be neutralized to ease further processing.

This paper will focus on impurities in barium titanate powders as interpreted by x-ray photoelectron spectroscopy (XPS) and x-ray diffraction (XRD). To understand the effect of processing on the surface of the powder, XPS was used specifically because it gives direct measurements of surface atomic composition as well as surface chemical bonding information. Traditional methods of evaluating the chemistry of barium titanate powders establish a bulk barium/titanium atomic ratio by either x-ray fluorescence (XRF) or wet chemical analysis. However, these bulk methods cannot distinguish between the different phases of barium that may be present in the samples. In addition, bulk measurements may not reflect the true surface chemistry of the powder, especially in the case of high surface area, submicron powders where surface heterogeneities may be present. XRD is frequently used for phase analysis but is of limited value when amorphous phases or very small amounts of a phase are present, as is typical of a surface. Fourier transform infrared (FTIR) spectroscopy can be used to identify surface groups, but the data cannot be easily quantified.

The XPS technique uses low energy x-ray beams to ionize inner-shell electrons from the
surface of the sample (depths < 50 Å)

KE = hν - BE - φ - Wc

where KE = kinetic energy of the ejected electron, hν = x-ray excitation energy, BE = binding energy of the atom, φ = combined work function of the instrument and sample holder, and Wc = work required to overcome charging in the sample due to poor electrical conduction.

Elements exhibit binding energy peaks whose relative positions depend on the electronegativity of their surrounding atomic neighbors. These are the chemical shifts by which the bonding states of the element are identified. In the case of a phase mixture where more than one bonding state exists, the relative distribution of a particular element in each bonding state can be interpreted by curve fitting the binding energy peaks and computing the total peak area fraction for each bonding state. However, curve-fitting results are associated with a high degree of error, are not necessarily unique solutions, and thus might not have a physical meaning, especially when energy shifts approach the peak resolution of the instrument.

Finally, different electronic transitions of the same element can reveal compositional information at two different depths if the difference in kinetic energy between the transitions is large enough. A depth composition profile of barium is possible because of the large difference in kinetic energy between the 3d barium peaks at 475 eV and the 4d barium peaks at 1160 eV. The 475 eV Ba 3d3/2 transition has a maximum escape depth of 10-20 Å, which corresponds to the powder surface, while the 1160 eV Ba 4d transition has a maximum escape depth of 30-50 Å, which corresponds more to the bulk region of the particle.

Peak identification for ceramic powders is especially difficult due to sample charging, which prevents assignments based on absolute binding energy. Rough and/or chemically non-uniform surfaces can cause differential charging effects that shift the energy peaks nonlinearly. Referencing to the graphite C 1s peak or to the Au 4f peak is a standard technique for overcoming this problem. However, slight differences in values for the same material in different studies are common in the literature. Charging can also broaden peaks, leading to the false conclusion that multiple bonding states are present. Although the literature does not cite a Ba binding energy for barium titanate, XPS studies of barium and barium-containing compounds have been of recent interest due to ongoing research in the field of superconductors. Van Doveren and Verhoeven, in their work on XPS spectra of alkaline earth metals and their oxides, determined that the spin-orbital splitting between the Ba 4d3/2 and the Ba 4d5/2 doublet for Ba metal and single-crystal BaO samples ranges from 2.1 to 3.0 eV.

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Young and coworkers and Brow on 123 superconductors exposed to air demonstrated additional peaks at higher binding energies in the Ba 3d, O 1s, and C 1s spectra, but not in the Cu 2p and Y 3d spectra. Furthermore, Brow shows that these high binding energy peaks correspond to a spectra of a known BaCO3 sample with an O 1s peak at 531.4 eV, a Ba 3d3/2 peak at 780.1 eV, and a C 1s peak at 289.2 eV.

The binding energy shifts of barium can be explained by chemical bonding models. Barium is a highly electropositive element, and barium oxide compounds are nearly completely ionic. In these cases, the barium can be assumed to be in the 2+ state at all times. Chemical shifts are then primarily the result of local potential changes caused by different anion coordination. A higher coordination of negative ions would increase the local electron potential function, decreasing the measured binding energies of the photoelectrons. Assuming a perovskite-like structure for the 123 compound, the barium is 12-fold. In comparison, barium carbonate has 9-fold and barium hydroxide has only 8-fold coordination with oxygen ions. The 123 would be expected to have the lowest binding energies, with the barium carbonate and hydroxide having increasingly larger binding...
energies. Barium titanate has an oxygen coordination of twelve and is expected to have core photoelectron binding energies similar to 123 and thus lower than both barium carbonate and barium hydroxide.

2. Materials and Characterization

2.1 Powder preparation

Both a commercially available oxalate-derived barium titanate and various hydrothermally synthesized barium titanate powders were studied under XPS. The commercial powder was a high purity grade barium titanate (Ticon HPB, Lot #716, TAM Ceramics, Niagara Falls, NY) made by an oxalate coprecipitation process, calcined to 850°C, and spray dried.

Three partially reacted hydrothermal powder batches were prepared for initial XPS studies, each by mixing 20 g of reagent-grade hydrous barium hydroxide (Fisher Chemical, Fairlawn, NJ) with 5 g of reagent-grade titanium dioxide (Fisher Chemical, Fairlawn, NJ) in ambient atmosphere for an initial Ba/Ti molar ratio of 1. A slurry of the powder and 30 ml of deionized, double distilled water was reacted without stirring in a 90°C oven in a sealed 60 ml teflon reaction vessel (Savillex, Minneapolis, MN). The slurry from a different batch was taken out of the oven after 1, 4, 12, and 56 h. Each slurry was diluted with 100 ml of 1 M formic acid and vacuum filtered with 0.2 μm pore polyvinylidene difluoride filter paper (Millipore Corp., Bedford, MA) until dry. The filter cake was oven dried in air at 90°C.

More fully reacted batches of hydrothermal powder with an initial Ba/Ti ratio of 1.1 were prepared for rinsing studies in a similar fashion by mixing 29 g of barium hydroxide with 6.7 g of titanium dioxide in sealed 90 ml teflon reaction vessels (Savillex, Minneapolis, MN). After 72 h the slurry was vacuum filtered without dilution with 0.2 μm pore polyvinylidene difluoride filter paper (Millipore Corp., Bedford, MA) until dry. To minimize reactions between the powder and atmospheric carbon dioxide and possible hydrothermal reactions in a drying oven, freeze drying (Dura-Dry, FTS Systems, Stone Ridge, NY) was employed instead of oven drying as before.

2.2 Characterization

The hydrothermal and commercial barium titanate powders were characterized by XRD, XRF, and XPS. Quantitative x-ray analysis (XRD) was performed via a matrix flushing method on an automated diffractometer (Model D-500, Siemens AG, Karlsruhe, FRG) using Ni-filtered Cu K-alpha radiation and operated at 40 kV, 30 mA, with zircon as the internal standard. The data were collected by means of a Daco (Siemens AG, Karlsruhe, FRG) microprocessor using a stepwidth of 0.04 degrees 2θ and a measuring time of 2 s per step for the barium titanate peak and 10 s per step for the other minor peaks. Bulk XRF measurements of samples of the hydrothermal powder were conducted at E. I. du Pont de Nemours using wavelength dispersive spectroscopy in conjunction with a proprietary analysis method. Two replicate fused samples were examined for Ba, Sr, and Ti content. These same samples of hydrothermal powder were also examined by XPS.

For XPS analysis, powders were tightly packed into a shallow depression in an aluminum sample stub with a glass slide to avoid spurious signals from commonly used adhesives. The samples were then gradually degassed in the sample introduction chamber and placed into the high vacuum chamber of the XPS spectrometer (XSAM-800, Kratos, Ramsey, NJ) for examination. The electron signal was generated by nonmonochromated Mg K-alpha radiation produced from a Mg anode under 16 keV and 15 mA. The spectra were collected with a spot size of 2 mm × 2 mm to minimize the signal from the sample stub using a hemispherical electron energy analyzer with a bias setting of 5.0 eV. Powders were found to contain barium, titanium, oxygen, and carbon peaks. However, only the barium 3d and 4d spectra were extensively analyzed and quantified due to poor peak resolution and high noise levels in the other spectra. The signal curves for the various barium bonding states were fitted by peak addition using Gaussian peak approximations and Shirley background reduction.

For the quantitative barium bonding state analysis, all the overlapping barium peaks were fitted by peak addition methods that incorporated an energy shift of 1.4-1.6 eV between each barium bonding state in the spectra and a rough d₃₋₂ to d₃₊₂ intensity ratio of 3:2. This interval and intensity ratio were determined by
extensive analysis of peak shift trends in over twenty different barium titanate samples as well as a barium carbonate standard. Because barium carbonate and barium hydroxide have similar coordinations, to simplify calculations these impurity phases were added together as one barium impurity state to be distinguished from the barium titanate bonding state in the powder. Since the area under each peak corresponds to the concentration of a particular bonding state, the percentage of total peak area under the barium titanate doublet was taken to correspond to the percentage of the total moles of barium detected by XPS in a barium titanate bonding state. This calculated number reflected the mole percent of barium detected in a barium titanate chemical bonding state for each sample. The percentages calculated from the above mentioned curve-fitting routines had an uncertainty of roughly ±5 mol%.

3. Results and Discussion

In general for the XPS barium spectra, two sets of doublet peaks, each corresponding to a different chemical bonding state, were found for both the 3d (Fig. 1) and 4d Ba transitions. The chemical shift between the bonding states ranged from 1.4-1.6 eV for both the Ba 3d and Ba 4d transitions. The Ba 3d peaks had an average full width half maximum (FWHM) of 2.2 eV, while the Ba 4d peaks were narrower, having an average FWHM of 1.5 eV. The spin-orbital splitting for the Ba 3d transition was found to be @15 eV, allowing separate windowing of each of the Ba 3d doublet peaks. The spin-orbital splitting for the Ba 4d transition, however, was found to be only @2.5 eV, which is in agreement with 123 work by Ford et al. Using methods discussed previously, analysis of the barium spectra identified the lower binding energy peaks as lattice barium titanate and the higher binding energy peaks as barium carbonate and/or barium hydroxide. Considering the aqueous thermodynamic stability of barium carbonate in contact with air, the presence of barium carbonate would be expected in these samples12). As analyzed by XPS, barium titanate powders in contact with air apparently have a surface layer of barium carbonate or some other lower coordination barium impurity.

Support for our peak assignment analysis was provided by other experimental data. First, a wide variety of commercial and hydrothermal powders have all followed the same general trends described above. Second, XPS and XRD studies of the partially reacted hydrothermal samples showed that an increase in barium titanate bonding state detected by XPS corresponded to an increase in crystalline barium titanate phase detected by XRD, as shown in Fig. 2.

Analysis of our XPS data provided information on a barium impurity phase faintly present or absent by other characterization methods (Table 1). A common characteristic of all the barium titanate powders analyzed with XPS
was that the percentage of barium in a barium titanate bonding state was 80 mol% or less, with the barium impurity phase accounting for the rest of the barium signal. The @ 1:1 (BaO + SrO)/TiO₂ molar ratios detected by XRF and low impurity levels detected by XRD are typical of what one would expect if the impurity phases were amorphous or concentrated in the near surface region. Comparing hydrothermal powder batches 1 and 2, it is interesting to note that the XRF (BaO + SrO)/TiO₂ molar ratios, 1.016 and 1.021, inversely scale with the corresponding XPS Ba 4d data, 74 and 61 mol% BaTiO₃. These data indicate that as the powder became richer in barium, the additional barium was incorporated into an impurity phase.

XPS was also capable of resolving the spatial nature of the impurity phase. Comparison of

<table>
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<th>Analysis method</th>
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<th>Batch 1</th>
<th>Batch 2</th>
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* XRF data from manufacturer
# (BaO + SrO)/TiO₂ molar ratio

the Ba 3d and 4d data in Table 1 reveals that consistently less barium in a barium titanate bonding state was detected for the Ba 3d transition than the Ba 4d transition. For instance, Batch 2 was found to have a bonding state proportion of 47 mol% BaTiO₃ for the Ba 3d transition, while this increased to 61 mol% BaTiO₃ for the Ba 4d transition. It is also interesting to note that the magnitude of the 3d barium titanate levels for the hydrothermal powders (approx. 47-50 mol% BaTiO₃) are within experimental error of the curve-fitting routine and thus are indistinguishable. The similarity of the 3d peaks and the contrasting nature of the 4d peaks described earlier suggest that the thickness of the impurity phase is greater than the escape depth of the Ba 3d electrons (< 20Å) but less than that of the Ba 4d electrons (< 50 Å). This impurity phase may be present either as a surface layer or as a barium impurity phase occluded within microporous regions of a porous barium titanate particle.

4. Conclusion

XPS studies have revealed that a barium titanate bonding state can be distinguished from a non-barium titanate bonding state on the basis of the barium peak shifts. The non-barium titanate bonding state has been assigned a peak located 1.5 eV higher in binding energy than the barium titanate peak for both the 3d and 4d barium transitions. Further studies have shown that barium titanate powders exposed to air have a significant amount of barium-rich surface impurity phases undetectable by XRD or XRF. Ongoing work with XPS is investigating...
the effect of postsynthesis processing, such as rinsing procedures, on the surfaces of sub-micron barium titanate powders.

Acknowledgments

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References